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Ordering dependence of carrier lifetimes and ordered states of $Ga_{0.52}In_{0.48}P/GaAs$ with degree of order $\leqslant 0.55$

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Photoluminescence (PL) properties and carrier lifetimes of spontaneously ordered $Ga_{0.52}In_{0.48}P/GaAs$ are measured at low temperatures. Samples with values of degree of order S from 0.22 to 0.55 are used. The full width at half maximum of the PL increases from 9.36 to 30.6 meV with increasing S. The PL peak of the indirect transition is blueshifted with increasing excitation power, whereas the PL peak of the direct transition is not. The energy separation between the PL peaks for the direct and the indirect transitions becomes greater with increasing S. The carrier lifetime increases dramatically with increasing S, from 0.68 ns at $S=0.22$ to 13 800 ns at $S=0.55$ at the peak energy of the PL spectrum. The ordering dependence of these characteristics is interpreted using a simple physical model of the ordered state. Variations in the ordered state with increasing ordering are discussed. © *2001 American Institute of Physics.*
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I. INTRODUCTION

The atomic arrangement in an alloy semiconductor generally exhibits short-range order, but not long-range order.[1,2] However, a long-range ordered arrangement may appear spontaneously during epitaxial growth of an alloy semiconductor with specific values of composition, particularly 1/4, 2/4, and 3/4 for a zincblende crystal structure. The long-range ordered arrangement significantly influences the electrical and optical properties.[3–9]

Under certain growth conditions,[10–13] $Ga_{0.52}In_{0.48}P$ lattice matched to GaAs is in an ordered state with CuPt-type long-range ordering on the group III sublattice. Ga and In atoms occupy alternating {111} planes to form a (GaP/InP) monolayer superlattice. Complete disordering means Ga and In atoms mix randomly, giving no long-range ordering, and perfect ordering would constitute a monolayer superlattice throughout the $Ga_{0.52}In_{0.48}P$ sample. The degree of order S varies from $S=0$ for completely disordering to $S=1$ for perfect ordering. As the degree of order increases, far-field photoluminescence (PL) spectra shift to longer wavelengths. This indicates that band gap of the ordered state is lower than that of the disordered state. The carrier lifetime is an important property to evaluate the luminescence processes in semiconductors and thus to evaluate device applications. It has been observed that ordered $Ga_{0.52}In_{0.48}P$ exhibits long lifetimes.[14]

In this study, we investigate the PL properties and the ordering dependence of the carrier lifetimes for a range of S from 0.22 to 0.55. From these experimental results, variations of the band structure as a function of the degree of order are discussed.

II. SAMPLE PREPARATION

The GaInP epitaxial layers were grown by organometallic vapor phase epitaxy on the (001)-surface of semi-insulating GaAs substrates misoriented by an angle of 9° or 3° toward the [1 1 0] direction. The growth was carried out in a horizontal, atmospheric pressure reactor using trimethylgallium (TMGa), trimethylindium, and phosphine. The growth temperature was 670 °C. Before beginning the GaInP growth, a 0.15 μm GaAs buffer layer was grown using TMGa and arsine to improve the quality of the GaInP layers. The thickness of the GaInP layer was 3000 Å. The input partial pressure of phosphine was varied under a constant flow rate of the group III gases to grow ordered layers with different values of S.[15] The terrace width on substrates inclined by an angle of 9° becomes relatively narrow, which suppresses the growth of the double periodic CuPt-type ordered structure. Thus, the grown layers tend to be in a disordered state. Spontaneous ordering along the [1 1 1] direction is promoted on substrates inclined by an angle of 3°. Table I summarizes the samples used in this study. Here, the degree of order S is calculated from the equation[16]

$$\varepsilon_g = \varepsilon_g(S=0) - \Delta\varepsilon_g S^2,$$

where ε_g denotes the measured energy band gap, $\varepsilon_g(S=0) = 2.005$ eV the energy band gap of a complete disordered state, and $\Delta\varepsilon_g = 0.471$ eV. These are values experimentally determined at 2 K.[17]

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TABLE I. $Ga_{0.52}In_{0.48}P$/GaAs samples grown at 670 °C by organometallic vapor phase epitaxy. Here, P_V represents the partial pressure of phosphine and S the degree of order.

Sample No.	Substrate	Thickness (Å)	P_V (Torr)	S
54	(001)→9°[1$\bar{1}$1]	3000	3	0.22
125	(001)→3°[1$\bar{1}$1]	3000	0.75	0.42
52	(001)→3°[1$\bar{1}$1]	3000	3	0.45
56	(001)→3°[1$\bar{1}$1]	3000	6	0.49
45	(001)→3°[1$\bar{1}$1]	3000	12	0.54
46	(001)→13°[111]	3000	18	0.55

III. EXPERIMENTS

The PL was excited with a He–Cd laser. The surfaces of all samples were passivated by ammonia sulphide before the measurements. The time-resolved photoluminescence (TRPL) measurements were performed with a fast scan streak camera in conjunction with a 25 cm monochromator using a 300 lines/mm grating. Pulsed excitation was provided by the frequency doubled beam of a mode-locked Al_2O_3:Ti laser which was pumped by an Ar+ laser. In order to avoid multiexcitation, the repetition rate of the source (80.0 MHz) was selected to one of 4.0 MHz, 400 kHz, or 80 kHz by the acoustic optic modulator. The lower repetition rate was used for the longer carrier lifetimes. The wavelength and the pulse width were 400 nm and 1.5 ps, respectively, by which selective excitation of the $Ga_{0.52}In_{0.48}P$ can be achieved. The excitation power density was kept constant at about 100 nJ/cm^2.

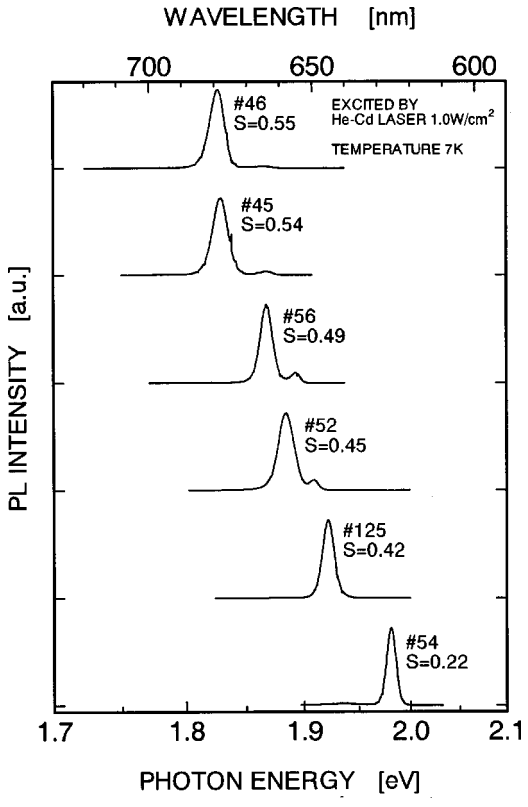

FIG. 1. Photoluminescence (PL) spectra of $Ga_{0.52}In_{0.48}P$/GaAs at 7 K.

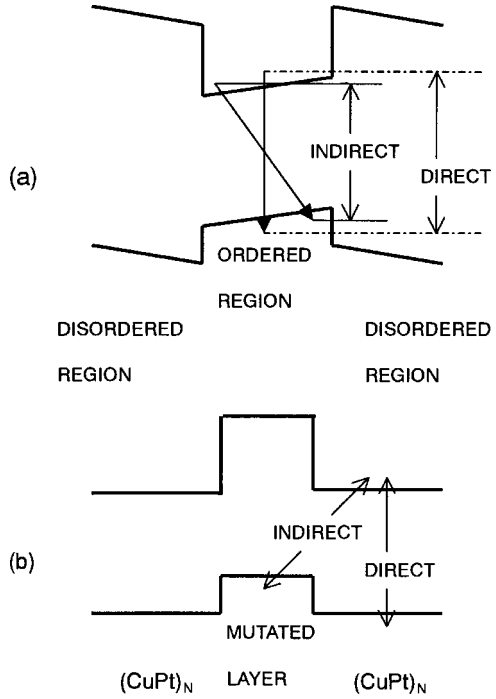

FIG. 2. Illustration of direct and indirect transitions in an ordered $Ga_{0.52}In_{0.48}P$/GaAs. (a) Energy band structure by disordered and ordered regions. (b) Energy band structure by $(CuPt)_N$ and mutated layers (Ref. 19). Here N denotes the thickness of the CuPt region.

IV. EXPERIMENTAL RESULTS

A. Photoluminescence

PL spectra of all samples at low temperature (7 K) are shown in Fig. 1 where two peaks were clearly observed except for No. 54 ($S=0.22$) and No. 25 ($S=0.42$). The peak at the lower energy side is strong and that at the higher energy side weak. The former has been identified as the luminescence from an indirect transition where a spatial separation is caused by a piezoelectric field[18] and/or the type II of the energy band alignment.[19] The latter is from the direct transition in an ordered state. Both processes are shown schematically in Fig. 2. The full width at half maximum (FWHM) of the PL spectra of the indirect transition is shown in Fig. 3, where it increases from 9.36 meV at $S=0.22$ to 30.6 meV at $S=0.55$. The temperature variations of the PL peaks of sample No. 56 are shown in Fig. 4. The PL peak of the direct transition shifts to a higher energy side and then follows fairly well to Varshni's equation[20] beyond about 25 K. It indicates the PL by excitons and they break at near 25 K. The PL peak of the indirect transition also shifts to the higher energy side and then to the lower energy side beyond about 50 K.

PL spectra were measured at 7 K by changing the excitation power and the observed results are shown in Fig. 5. The results of sample No. 56 ($S=0.49$) show that the PL peak from the direct transition does not shift, whereas the PL peak from the indirect transition makes a blueshift with increasing excitation power. A blueshift of 5.7 meV occurs when the power is increased from 3.4×10^{-4} to 1.0 W/cm^2.

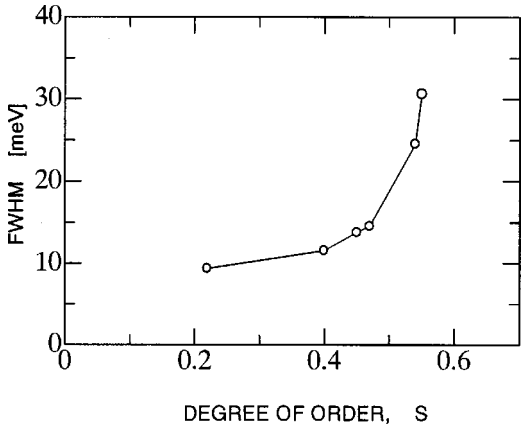

FIG. 3. FWHM of PL spectra for the indirect transitions at 7 K as a function of degree of order.

The PL peak energy versus excitation power is shown in Fig. 6. The energy separation between PL peaks from the direct and indirect transitions becomes large for $S>0.4$, as shown in Fig. 7. The separation is small for a lower value of S. Here the small negative values are due to experimental errors.

B. TRPL

TRPL for the indirect transition was measured at 20 K, and the PL intensity decays fast with time t at first and then slowly. The decay characteristic can be approximated to be exponential as $\exp(-t/\tau)$ where τ is identified as the carrier lifetime. The fast decay portion is described by $\exp(-t/\tau_f)$ and the slow by $\exp(-t/\tau_s)$, where τ_f and τ_s are the fast and the slow carrier life times, respectively.

The ordering dependence of the fast and the slow lifetimes at the peak value of PL intensity is shown in Fig. 8. They increase exceedingly with S, from $\tau_f=0.118$ ns and $\tau_s=0.450$ ns for $S=0.22$ to $\tau_f=2690$ ns and $\tau_s=13\,800$ ns for $S=0.55$.

The carrier lifetimes, fast and slow, become longer as the wavelength is moved from the high energy side to the low energy side of a single PL spectrum. The slow carrier lifetime is considered as being influenced by energy band edges. In Fig. 9, variations of the slow carrier lifetimes in individual PL spectra are shown. The decay of PL intensity can be expressed almost by a single carrier lifetime rather than the two, fast and slow, when the carrier lifetime becomes very long. The discontinuous changes appearing for $S\geqq 0.45$ are an indication of the transition from the situation where the PL intensity decays with a single lifetime.

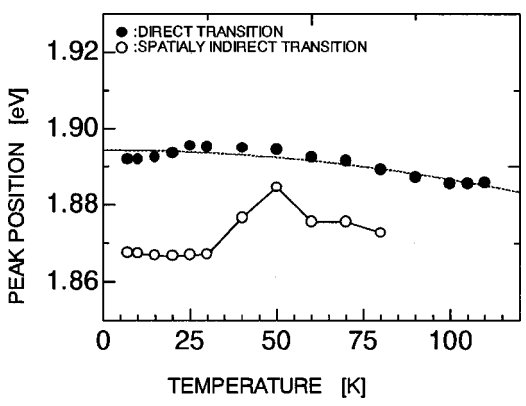

FIG. 4. Temperature variation of PL peak for sample No. 56.

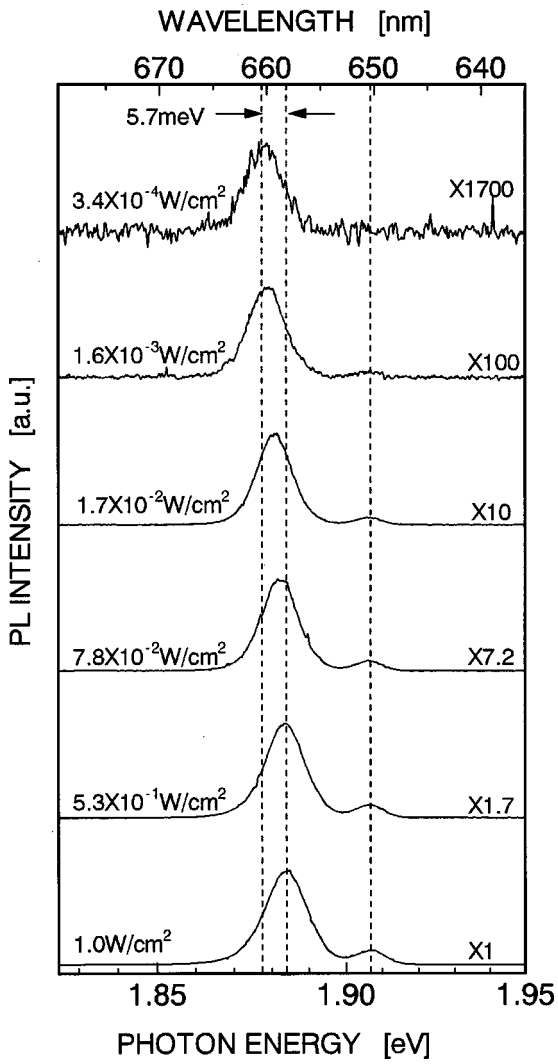

FIG. 5. PL spectra of sample No. 56 at 7 K with changing excitation power.

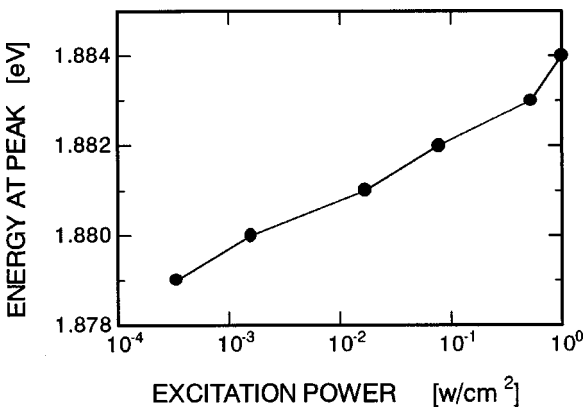

FIG. 6. Energy shift of PL peaks from indirect transitions at 7 K with increasing excitation power.

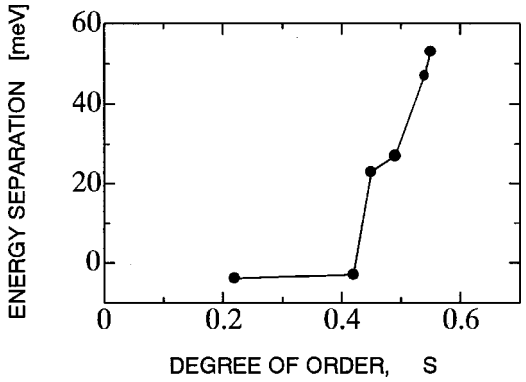

FIG. 7. Energy separation between PL peaks from direct and indirect transitions vs degree of order.

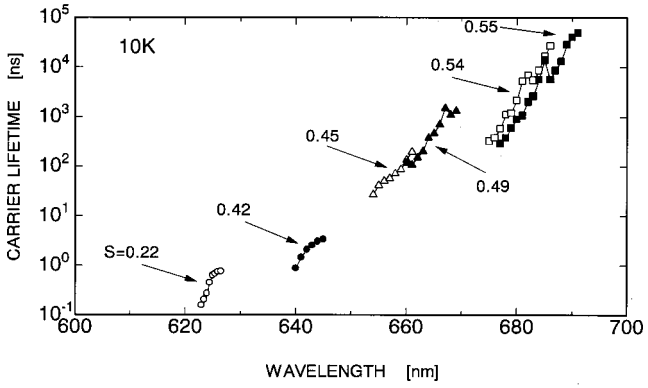

FIG. 9. Slow carrier lifetimes in PL spectra at 20 K as a function of degree of order.

V. ORDERED STATE AND DISCUSSION

We first present a physical model for the ordered state of the alloy semiconductor $Ga_{0.52}In_{0.48}P$ and then interpret the experimental PL and TRPL characteristics. In the past, a variety of experiments and physical models to understand the ordered state of $Ga_{0.52}In_{0.48}P$ have been reported.[14,18,19,21–26] However, the ordered state has not been fully revealed yet and this remains a major issue for ordered alloy semiconductors. To understand an ordered alloy semiconductor, the size and shape of the ordered region are important. In addition their variations and spatial distributions are important as well as functions in degree of order. Such features cannot be clearly and individually described, but are better described statistically.

Growth and substrate surface conditions determine the degree of order. Under a particular set of growth conditions and for a perfectly uniform substrate surface, the atomic alignment in the epitaxially grown layer could be considered to be uniform, with a particular value of degree of order. However, due to fluctuations in growth conditions, such as in gas flow, gas partial pressure, growth temperature, etc., and the inherent nonuniformity of the substrate surface, the atomic alignment in the alloy becomes nonuniform. Thus, we expect: (1) highly ordered arrangement as well as less ordered arrangement and (2) the antiphase boundary between the ordered regions appear in the epitaxial layer. This deviation from uniformity is difficult to evaluate. Here, we greatly simplify the description of the spontaneously ordered alloy by assuming it is composed of completely uniform disordered and perfect (long-range) ordered portions.

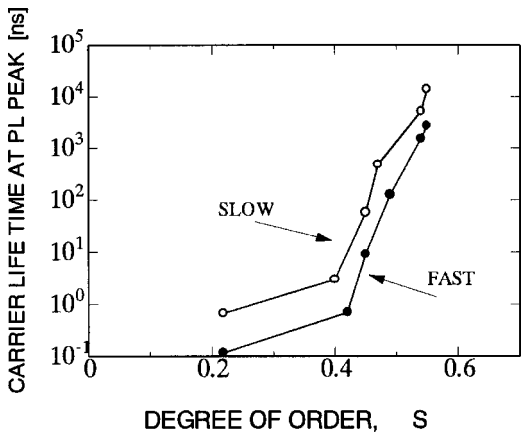

FIG. 8. Ordering dependence of fast and slow carrier lifetimes at the peak value of PL at 20 K due to indirect transitions.

The ordered state is assumed to form under a thermal quasiequilibrium.

(a) The shape is symmetric in configuration space. In actuality, the shapes become arbitrary due to the existence of defects in a semiconductor.

(b) The spatial distribution is uniform. It is not completely uniform because of defects.

(c) The degree of order is considered to be constant within the ordered state. It was observed by low-temperature near-field PL that the degree of order S varies by only about 1% within the area of radius $\sim 250\ \mu$m.[24] In this extremely simplified model, the degree of order is basically the volume fraction of ordered material.

(d) The size distribution is Gaussian. However, we do not know the average size. A standard deviation σ of the distribution is considered as $\sigma \leqq S \leqq 0.5$. Beyond $S \fallingdotseq 0.5$, it would be better to consider a disordered state in an ordered matrix.

(e) Ordered and disordered regions are concluded in theory to form a type I quantum structure.[18,20] However, electrons and holes are separated in configuration space due to the piezoelectric field, i.e., under the quantum confinement Stark effect. The structure can be a quantum dot or disk in three-dimensions.

From this very simple physical model of an ordered state, the following can be stated:

(i) The size deviation increases with the degree of order and becomes a maximum near $S = 0.5$.
(ii) The average size also increases with the degree of order.

From (i), the PL FWHM of the indirect transition becomes wider with the degree of order, as seen in Fig. 3. The change of the peak position for the indirect transition PL with temperature, seen in Fig. 4, would be considered as being partly due to the screening of the piezoelectric field and the band filling effect by the increase of carrier concen-

tration in the ordered region. Above 50 K, the band gap of the ordered state decreases as in Varshini's equation. This presumption must be examined further due to the change in the carrier concentration with temperature.

Increasing the excitation power causes an increase in carrier concentrations which screen the piezoelectric field. Thus, the peak of the indirect transition PL shifts to higher energy describing the blueshift seen in Figs. 5 and 6.

From (ii), the separation of electrons and holes becomes wider with increasing degree of order. As the size of the ordered state becomes large, the effective band gap becomes smaller due to the piezoelectric field. Thus, the energy separation between PL peaks from the direct and the indirect transitions becomes large as seen in Fig. 7. As the carrier separation becomes greater, with increasing S, the carrier lifetime becomes longer, as seen in Figs. 8 and 9.

We can predict that the PL FWHM will become narrower and the carrier lifetime shorter beyond $S \fallingdotseq 0.5$. We have observed these characteristics in the sample with $S = 0.64$. The result will be reported elsewhere. This is reasonable because the PL FWHM and the carrier lifetime cannot increase continuously beyond $S \fallingdotseq 0.5$. They must converge to the values of a perfect ordered monolayer superlattice of (GaP/InP). When they are greater than those of a complete disordered alloy, the widest PL FWHM and the largest carrier lifetime occur at greater than $S = 0.5$.

Recent theoretical works have shown that the energy band alignment is type II for an ordered $Ga_{0.48}In_{0.52}P/GaAs$.[19] Experimental results here could be also interpreted by the type II energy band alignment, when the length of mutated layers, the thickness of the CuPt region, and the piezoelectric field depending on the degree of order are thoroughly investigated.

VI. SUMMARY

In summary, we have measured the ordering dependence of PL properties and the carrier lifetime systematically from the degree of order $S = 0.22-0.55$. The FWHM of the PL increases with the degree of order: from 9.36 to 30.6 meV. The PL peak of the indirect transition makes a blueshift with increasing excitation power: for example, a 5.7 meV shift is seen as the power increases from 3.4×10^{-4} to 1.0 W/cm^2 at 7 K. The energy separation between the PL peaks of the direct and the indirect transitions increases with the degree of order: from close to zero for $S = 0.22$ to 55 meV for $S = 0.55$. The carrier lifetime increases dramatically with increasing S: from the fast carrier lifetime $\tau_f = 0.118$ ns and the slow carrier lifetime $\tau_s = 0.450$ ns to $\tau_f = 2690$ ns and $\tau_s = 13\,800$ ns.

These characteristics have been interpreted using a simplified physical model of the ordered state in which the size deviation and an averaged size increase in proportion to the degree of order S for approximately less than 0.5.

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